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(54) Title: ELASTOMERIC ARTICLES

(57) Abstract: An elastomeric article has a laminate structure and is comprised of outer layers of a polyurethane composition and an inner layer of a styrene-isoprene-styrene (SIS) or a styrene-butadiene-styrene (SBS) block copolymer or a blend thereof. The article may for example be a glove, condom, urinary sheath or catheter and may be produced by dipping a former successively into a solution or suspension of a polyurethane, then into a solution or suspension of an SIS or SBS block copolymer, followed by dipping into a solution of a polyurethane (with drying as necessary between the dipping stages) to build-up the laminate structure during formation of the article.

## ELASTOMERIC ARTICLES

The present invention relates to elastomeric articles, particularly but not exclusively gloves and condoms, and also to a method for the production of such articles.

There are many common elastomeric articles such as gloves (e.g. for medical applications such as examination or surgery) and condoms. Such articles may be produced by dipping a suitably shaped former into a solution or suspension of the elastomeric material, withdrawing the former from the solution/suspension and evaporating the carrier liquid of the solution/suspension. More than one dipping process may be used to produce the final article.

Requirements for the elastomeric articles are that, in addition to having the required elastomeric properties, they should be resistant to materials with which they come into contact and should have good resistance to oxidation to provide for a reasonable shelf-life of the article. Given that many articles intended for use in biomedical applications require sterilisation by  $\gamma$ -irradiation the oxidation resistance of the material to be used is of particular importance.

For many years, the material of choice for such applications has been vulcanised natural rubber (NR) latex (the polymeric component of which is cis-polyisoprene) due to the excellent balance of softness, strength and elasticity exhibited by articles fabricated from it.

The use of NR-latex is by no means ideal however due to the presence of latex proteins and accelerator residues from the vulcanisation process. These chemicals often bloom to the surface of the fabricated article and may be adsorbed within the tissues of a user, thereby causing an allergic response. The problem is particularly serious with allergies to latex protein and a (protein free) synthetic substitute to NR latex is urgently sought.

NR latex also suffers from a low resistance to oxidation due to the unsaturated carbon-carbon double bonds present within the cis-1,4-isoprene repeat units within the polymer. This may be mitigated to some extent by the inclusion of anti-oxidants within a formulation to be used for fabricating articles but the anti-oxidants also bloom to the rubber surface and produce an allergenic or cytotoxic response.

One synthetic elastomeric material that has been used is S-EB-S (a styrene / ethylene- butylene / styrene triblock co-polymer) which has the required elastomeric properties and good resistance to oxidation (Shell technical literature "Kraton Polymers For Adhesives And Sealants"). Thus, for example, US-A-5,112,900 describes an elastomeric composition formed from two or more S-EB-S triblock copolymers, which composition has a combination of strength, tactility and resistance to environmental attack.

However, S-EB-S copolymers are typically harder than NR latex and require plasticisation to make them suitable for certain product applications. Thus, the composition disclosed in US-A-5,112,900 incorporates a mineral oil as a plasticiser. The inclusion of a plasticiser in a medical device is not ideal as the plasticiser may migrate over time and give rise to a leachable component yielding deleterious side effects when the device is used.

Further materials that have been used as elastomeric articles are SIS (a styrene / isoprene / styrene co-polymer) and SBS (a styrene / butadiene / styrene co-polymer), both of which have an ideal combination of strength, elasticity and softness. Thus, for example, EP-A-0 854174 describes a method of forming powder-free elastomeric gloves from a mixture of a SIS triblock copolymer with a SBS triblock copolymer and an anti-blocking additive, and EP-A-0 931633 discloses a further method of forming a powder-free glove from a synthetic rubber which may be a styrene block copolymer or polychloroprene by applying an elastomeric latex coating to the glove.

However, both SIS and SBS copolymers have, by dint of carbon-carbon unsaturated bonds within their structure, poor resistance to oxidation and this

deleteriously affects the shelf-life of elastomeric articles produced therefrom. Neither of the European patent specifications identified in the previous paragraph improve the poor ageing characteristics of an SIS or SBS based elastomeric article. The manufacturers of SIS or SBS block copolymers include a variety of anti-oxidants to alleviate this problem but this impacts upon their suitability for biomedical applications as the potential for side effects caused by leechable components is to be avoided.

A further problem of preparing elastomeric protective articles is that the article can adhere to the surface of the former on which it is produced. As the article is typically of the order of 50-250 $\mu$ m thick, it is difficult to remove the article from the former without ripping or tearing. Obviously the presence of any imperfections, however minor, in an elastomeric article is to be avoided.

In addition NR latex and elastomeric SIS or SBS block copolymers tend to suffer from blocking (the tendency of the elastomeric article to adhere to itself) after being stripped from the former. Indeed this is such a problem with SIS and SBS block copolymers that certain grades are supplied as pellets dusted with powder.

In order to overcome the problems set out in the previous paragraphs, it is conventional to use a powder, either in a coagulant dip such that powder is deposited on the former (for glove manufacture) or in a slurry after the article is removed from the former (for gloves and condoms). There are many examples of powders that may be used for this purpose, such as magnesium carbonate or corn starch to prevent the elastomeric composition from adhering to itself after removal from the former and to facilitate removal of the article. The use of such powder does however increase the cost and complexity of the manufacturing process and if use is intended for an application involving contact with internal body fluid (as in the case of catheters, condoms and surgeons gloves) there is a risk that the powder may cause granuloma. In addition a powdered article could not be used for an application wherein a requirement for minimal contamination existed (such as an examination glove for procedures within a clean room environment).

It is an object of the present invention to obviate or mitigate the above disadvantages.

According to a first aspect of the present invention there is provided an elastomeric material having a laminate structure and being comprised of outer layers of a polyurethane composition and an inner layer of a styrene-isoprene-styrene (SIS) or a styrene-butadiene-styrene (SBS) block copolymer or a blend thereof.

The term "polyurethane" as used herein is intended to include polyurethane-ureas.

The material is preferably a tri-laminate structure comprised of an inner SIS or SBS layer or blend thereof and outer polyurethane layers but we do not preclude the possibility of there being at least one further inner layer.

The laminate material of the invention has excellent resistance to oxidation. Without being bound by theory we believe this is due to the polyurethane layers acting as a barrier to oxidation of the SIS/SBS layer and/or as a barrier to migration of anti-oxidant from the SIS/SBS layer. An additional advantage is that the material has a reduced tendency to "blocking". This is due to the fact that the polyurethane is a "harder" material than the SIS/SBS layer. This difference in hardnesses means that reduced quantities of blocking agents may be used in the polyurethane layers so as to avoid "blocking", with less possibility that the anti-blocking agents migrate out of the polyurethane layer and the need for powders such as magnesium carbonate or corn starch can be avoided. Furthermore, the SIS or SBS layer provides properties of strength, elasticity and softness, and these properties are complemented by the outer polyurethane layers so that the material is eminently suitable for use in producing elastomeric protective articles.

According to a second aspect of the present invention there is provided an elastomeric article comprised of an elastomeric material as defined for the first aspect of the invention.

The article may, for example, be a glove, a condom, a catheter or a urinary sheath. The glove may be for medical use and may, for example, be for use in medical examination or surgery. There are standards governing the physical properties of certain of these articles (e.g. ASTM 3577 for surgeons gloves) whereas other articles (such as examination gloves or urinary sheaths) are not subject to such a standard but good elastomeric properties and freedom from leechable chemicals are deemed highly desirable.

The laminate material of the first aspect of the invention may be produced *in situ* during formation of an article in accordance with the second aspect of the invention. Thus, for example, the article may be produced by dipping of a suitably shaped former firstly into a solution or suspension of a polyurethane, then into a solution or suspension of an SIS or SBS block copolymer, followed by dipping into a solution of a polyurethane (with drying as necessary between the dipping steps) to "build-up" the laminate structure during formation of the article.

It is however also possible for the material of the first aspect of the invention to be produced in the form of a sheet or the like which is subsequently used for manufacture of an article in accordance with the second aspect of the invention.

Preferably the SIS or SBS layer has a thickness of from 30 to 1,000 $\mu$ m, more preferably from 40 to 300 $\mu$ m, most preferably from 50 to 200 $\mu$ m.

Preferably the polyurethane outer layers have a thickness of from 2 to 100 $\mu$ m, more preferably from 5 to 50 $\mu$ m, most preferably from 10-20 $\mu$ m.

In use it is envisaged that in certain applications (such as surgeon's gloves and self lubricating condoms) the "inner" polyurethane layer, i.e. the layer that is in contact with the skin of the user, may be thinner than the "outer" layer of polyurethane to aid rapid swelling of absorbed moisture. In these cases it is preferred that the "inner" layer is more than or equal to one third of the thickness of the "outer" layer.

Preferably the SIS/SBS block copolymer is a thermoplastic ABA block copolymer elastomer. Preferably the styrene content of the SIS/SBS block copolymer is from 15 to 35% (by weight). Preferably the molecular weight (number average  $M_n$ ) of the SIS/SBS block copolymer is from 150,000 to 300,000, more preferably from 200,000 to 250,000.

Particularly suitable examples of SIS block copolymers for use in the invention include Kraton D-1161 and 1107 (available from Shell Chemicals, which are styrene/isoprene triblock copolymers with 15% bound styrene) and Vector 4113 (available from Dexco Polymers). A further example of a SBS block copolymer for use in the invention is Kraton D-1184 (available from Shell Chemicals, which is a styrene/isoprene triblock copolymer with 30% bound styrene).

Optionally a blend of SIS and SBS block copolymers may be used.

It is important that a non-powdered SIS/SBS block copolymer grade is used during the preparation of the SIS/SBS solution or suspension as the powder will become mobile and may compromise the "powder-free" properties of the dipped article.

A wide variety of polyurethanes may be used for the outer layers of the laminate provided, of course, that the elastomeric, flexible structure of the laminate is retained. Thus, for example, the polyurethane may be a hydrophilic polyurethane but more preferably will either comprise a mixture of a hydrophilic polyurethane and a hydrophobic polymer (e.g. a hydrophobic polyurethane) or will be a hydrophobic

polyurethane. The polyurethane composition of the two outer layers of the laminate may be the same or different. The exact nature of the polyurethane comprising each outer layer will be dependent upon the intended application of the fabricated article.

Preferably the polyurethane composition of at least one (and more preferably both) of the outer layers of the laminate is comprised of a mixture of a hydrophilic polyurethane and a hydrophobic polymer, particularly a hydrophobic polyurethane. The use of a mixture of a hydrophilic polyurethane and a hydrophobic polymer provides a composition which is wetted by water and also one which has greater resistance to alcohol solvents relative to hydrophilic polyurethanes *per se*. The composition is therefore particularly suitable for use in the manufacture of surgical gloves, which generally need to be donned onto wet or damp hands (immediately after the surgeon has "scrubbed-up") since the wetting by water facilitates such donning of the gloves. Furthermore, the alcohol resistance of the composition may be of importance if the surgeon donning the glove uses an alcoholic based disinfectant to apply either to his hands or to the outer surface of the glove as part of his "scrub-up" procedure.

For such a composition comprised of a blend of a hydrophilic polyurethane and a hydrophobic polymer (preferably a hydrophobic polyurethane) it is preferred that the composition is comprised of 20% to 60% by weight of the hydrophilic polyurethane and 40% to 80% by weight of the hydrophobic polymer. A composition comprised of about 30% of hydrophilic polyurethane and 70% of a hydrophobic polyurethane is particularly suitable.

Alternatively, one or both of the outer layers may contain a hydrophobic polyurethane as the sole polyurethane. Such a layer is suitable as the inner layer of a glove which is to be donned onto a dry hand. The hydrophobic polyurethane is useful in providing resistance against alcohol solvents.

Where resistance to alcohol solvents is not important, then one or both layers may contain a hydrophilic polyurethane as the sole polyurethane. An example of this



would be a self-lubricating condom wherein the outer surface would be comprised of a hydrophilic polyurethane whereas the inner layer may either be a blend of a hydrophilic and a hydrophobic polyurethane or a hydrophobic polyurethane alone.

As indicated previously, articles in accordance with the invention may be produced by a dipping process in which an appropriately shaped former is successively dipped into, firstly, a polyurethane-containing solution/suspension, secondly into a SIS or SBS containing solution/suspension, and thirdly into a polyurethane containing solution/suspension.

Preferably the polyurethane for "dipping" is present in the form of a solution, most preferably in a polar solvent. Preferred examples of such polar solvents include tetrahydrofuran, methyl ethyl ketone, dimethylformamide, dimethylacetamide, N-methyl pyrrolidone, dimethylsulphoxide, oleic acid amide or mixtures thereof. Dimethylformamide is most preferred.

Preferably the polyurethane solution comprises 5-20% by weight (e.g. 8 to 15%) of the polyurethane. The solution may also incorporate additional additives such as precipitated silica, which acts as an anti-block agent and although a particulate, it becomes trapped within the polyurethane film structure and renders a powder-free finish and fatty acid amides, such as oleamide, erucamide, stearamide, behanemide, ethylene-bis-oleamide, ethylene-bis-erucamide and ethylene-bis-stearamide, which serve to reduce the surface friction produced by the silica and to act as an anti-block in their own right. Oleamide (oleic acid amide) is the most preferred fatty acid amide. Precipitated silica, if used, will generally be present in the solution in an amount of 5-10% (by weight of the polyurethane content), whereas a fatty acid amide or mixture of fatty acid amides, if used, will be present in an amount of 1-10% (by weight of the polyurethane content). Additionally hard hydrophobic waxes such as Carnuba wax (available as Miwax 411 from Michelman Inc.) may be incorporated into the polyurethane solution to provide anti-blocking properties. Hard hydrophobic waxes, if used, will generally be present in the solution in an amount of

5-10% (by weight of the polyurethane content). A preferred dipping solution has the following composition:

Polyurethane	15wt%
Dimethylformamide	85wt%
Precipitated Silica	9wt% (based on polyurethane wt)
Oleic acid amide	5wt% (based on polyurethane wt)

For certain embodiments of the invention good results will be achieved if the initial and final dipping solutions are of different composition.

A particularly preferred initial dipping solution has the following composition:

Polyurethane	12wt%
Dimethylformamide	88wt%
Precipitated Silica	9wt% (based on polyurethane wt)
Oleic acid amide	5wt% (based on polyurethane wt)

A particularly preferred final dipping solution has the following composition:

Polyurethane	8wt%
Dimethylformamide	92wt%
Precipitated Silica	9wt% (based on polyurethane wt)
Oleic acid amide	5wt% (based on polyurethane wt)

The presence of one or more additives selected from the group including precipitated silica, fatty acid amides and hard hydrophobic waxes, allows the dipping process to be carried out without the use of a powder (such as magnesium carbonate or corn starch) to prevent adherence to the former.

The SIS or SBS is also preferably used in the form of a solution, most preferably in an aromatic solvent, most preferably toluene or xylene, although

solvents such as tetrahydrofuran may also be used. This "dipping" solution may, for example, contain 20-45% (by weight) by weight of the SIS or SBS block copolymer, more preferably 24-35% (by weight).

In cases wherein the SIS/SBS solution is based upon an aromatic solvent and if the polyurethane-containing solution incorporates a hydrophobic polyurethane, then it will generally be preferred that the SIS/SBS solution incorporates a relatively polar liquid which is miscible with the aromatic solvent. The use of such a polar liquid in the SIS/SBS solution has been found to prevent or inhibit mottling of the final article, possibly caused by incompatibility between the aromatic solvent of the SIS/SBS solution and the hydrophobic polyurethane. The polar liquid may be incorporated in the SIS/SBS solution in an amount of 5-20% by weight of the solution. Particularly preferred examples of such polar liquids include NN-dimethylamides, e.g. dimethylacetamide or dimethylformamide, ketones, e.g. butan-2-one or alcohols, e.g. propan-2-ol.

The SIS/SBS solution may, for example, comprise

SIS	28wt%
Toluene	60wt%
Dimethylacetamide	12wt%

It will generally be preferred that the first (polyurethane) layer applied to the former be relatively thin (e.g. no more than 20-30 microns). Such a thickness may be achieved by relatively slow withdrawal of the former from the polyurethane solution for formation of the first layer.

In the following examples the figures stated relate to dipping of an article into the polyurethane and SIS/SBS solutions cited above. Significant variation of the content of polymer within the solution with corresponding significant variation of the viscosity of the solution will have a dramatic effect on the dipping speeds. Similarly the drying temperatures and times relate to the solvents cited above. The figures cited

below are therefore only intended to be indicative of fabrication parameters for a glove dipped from the preferred formulations cited, obviously the overall size, weight and shape of the dipped article will govern *inter alia* the final conditions used.

In the first dipping stage the former is preferably removed from the fluid medium at from 0.05 to 5 mm per second, most preferably at from 0.2 to 1mm per second. In the second dipping stage the former is preferably removed from the fluid medium at from 0.5 to 10 mm per second, most preferably at from 2 to 5mm per second. In the third dipping stage the former is preferably removed from the fluid medium at from 0.2 to 15mm per second, most preferably at from 0.5 to 5mm per second.

Preferably the former is dried between each dipping stage. Drying is preferably carried out at from 80°C to 130°C.

Following the first dipping stage drying is preferably carried out for from 3 to 20 minutes, most preferably for from 8 to 12 minutes. Following the second dip drying is preferably carried out for from 5 to 25 minutes, most preferably for from 10 to 15 minutes. Following the third dip drying is preferably carried out for from 3 to 20 minutes, most preferably for from 8 to 12 minutes.

The type of former used to fabricate the dipped article depends on the nature of the article to be fabricated.

Thus for a glove the former may be porcelain, either of bisque (a form of porcelain which has been fired but not glazed) or of a glazed ceramic finish, optionally the surface finish may be roughened by sandblasting the former or spraying a roughened finish. For a condom, the former is preferably glass. For a urinary sheath the former may be ceramic, stainless steel, aluminium or glass.

Hydrophilic polyurethanes for use in accordance with the invention will generally have a soft block incorporating poly(ethyleneoxide) (ethylene glycol) units.

Such groups within the backbone of a polyurethane render the capability of water binding and enable the polymer to swell and transmit moisture vapour. Suitable hydrophilic polyurethanes will comprise hard and soft blocks with the latter incorporating poly(ethyleneoxide) units desirably having a molecular weight of at least 400 and preferably in the range 400 to 8000. Generally also the overall content of poly(ethyleneoxide) units in the hydrophilic polyurethane will be at least 10% by weight within the polyol mixture used to produce the softblock.

Hydrophilic polyurethanes for use in the invention may be step-growth polymers formed via the reaction of an organic diisocyanate ( $\text{OCN-R-NCO}$ ) and appropriate chemical species having two active hydrogen substituents capable of reacting with such diisocyanate groups. A suitable polyurethane may be formed by the initial reaction of an aliphatic or aromatic diisocyanate with a relatively low molecular weight polymer (MW 400-8,000, preferably 1,000-2,000) incorporating poly(ethylene oxide) units and having end groups comprising an active hydrogen species (e.g.  $\text{OH}$  or  $\text{NH}_2$ ), in the ratio of  $n+1$ :  $n$  moles respectively to form a pre-polymer.

Representative examples of such diisocyanates include:

(i) hexamethylene diisocyanate, 4,4 dicyclohexylmethane diisocyanate, isophorone diisocyanate, 4,4 diphenylmethane diisocyanate, toluene diisocyanate, 1,5 naphthalene diisocyanate, tetramethyl xylene diisocyanate, and mixtures thereof.

Representative examples of the relatively low molecular weight polymers that may be used include:

(ii) polyethylene glycol having terminal hydroxyl or amine functionality, a block co-polymer (AB, ABA etc) of ethylene glycol and a hydrophobic polyol (such as propylene glycol or polytetramethylene glycol) having terminal hydroxyl or amine functionality or mixtures thereof.

Such low molecular weight polymers (or mixtures thereof) as listed under (ii) may be used individually to react with diisocyanates to form a pre-polymer. Alternatively the low molecular weight polymers, e.g. as exemplified under (ii) above may be used in conjunction with a further low molecular weight (e.g. 250-8000, preferably 1000-2000) polyol not containing poly(ethylene oxide) units. Examples of such further polymers include:

(iii) polytetramethylene glycol, polypropylene glycol, polycaprolactone polyol, polyethylene adipate polyol, polytetramethylene adipate polyol, polyethylene-tetramethylene adipate polyol, polyhexamethylene adipate polyol, polyethylene-hexamethylene adipate polyol, polyhexamethylene carbonate glycol, polyethylene-hexamethylene carbonate glycol, and mixtures thereof. For the purposes of this definition the term polyol has been used to refer to a polyester material containing terminal hydroxyl functionality and glycol a polyether (or polycarbonate) material containing terminal hydroxyl functionality. In each of the above examples the terminal hydroxyl functionality may be replaced by terminal amine functionality.

The pre-polymer is then extended by reaction with a low molecular weight aliphatic compound comprising difunctional groups with active hydrogen species (e.g. OH or NH<sub>2</sub>) and a diisocyanate in the ratio of x:x-1 moles per mole of prepolymer. Such low molecular weight aliphatic compounds comprising difunctional groups with active hydrogen species may be either diols or diamines or alkanolamines, representative examples of which include:

(iv) ethylene glycol, diethylene glycol, triethylene glycol, 1,2 propylene glycol, 1,3 propylene glycol, 1,4 butane diol, 1,3 butane diol, 2,3 butane diol, 1,6 hexane diol, 2,5 hexane diol, and mixtures thereof.

(v) ethylene diamine, propane diamines, butane diamine, pentane diamine, 2, methyl pentane diamine, 1,4 cyclohexyl diamine or mixtures thereof.

(vi) ethanolamine.

In an alternative to the above described procedure, the prepolymer may be produced by reaction of  $n+1$  moles of the diisocyanate (e.g. as listed under (i)) with (n) moles of a polyether glycol as identified under (iii) above. The product of this reaction is then further reacted with 2 molar equivalents of a hydroxyl or amine terminated low molecular weight polymer containing poly(ethylene oxide) units such as exemplified under (ii) above (i.e. one mole of prepolymer is reacted with 2 moles of a poly(ethylene oxide) containing polymer)

The extension reaction of the prepolymer is then effected with a low molecular weight aliphatic compound having two active hydrogen substituents, e.g. as exemplified by compounds (iv)-(vi) above and a diisocyanate (such as exemplified by (i) above) in the ratio of  $x:x+1$  moles per mole of prepolymer.

The hydrophilic polyurethane will generally have a hard block content of 18-35%. Generally the hard block will be derived from an aromatic diisocyanate and a butane diol. The soft block will be derived from an aromatic diisocyanate and a polyethylene oxide of the type described above. The polyethylene oxide may be capped with amine groups.

Two such examples will be cited as examples in this specification. Hyphil 1 is an aromatic polyether-urethane, having a hard block content of 18-23% with a soft structure of both hydrophilic and hydrophobic polyols, the former having a molecular weight 2,000 and the latter of 1,000. Hyphil 2 is an aromatic polyether-urethane, having a hard block content of 20-24% with a soft structure of both hydrophilic and hydrophobic polyols each having a molecular weight of 2,000.

The hydrophobic polymer used in admixture with the hydrophilic polyurethane may for example be a hydrophobic polyurethane. The hydrophobic polyurethane will not contain any ethylene glycol units in the soft block structure. Units of short ethylene glycol units (as identified above) may be incorporated into the hard block of a polyurethane without producing a material with appreciable

hydrophilic properties providing that there are not longer chains of polyethylene glycol in the soft block of the material.

Hydrophobic polyurethanes for use in the invention may be produced by initial formation of a prepolymer from  $n+1$  moles of an organic diisocyanate (such as exemplified by the compounds listed under (i) above and  $n$  moles of a compound having a hydrophobic moiety and two active hydrogen substituents, e.g. as exemplified by the compounds listed under (iii) above.

The pre-polymer may then be extended by reaction with a low molecular weight aliphatic compounds comprising difunctional groups with active hydrogen species (e.g. OH or  $\text{NH}_2$ ) (e.g. as exemplified under (iv)-(vi) above) and a diisocyanate (e.g. as exemplified by (i) above) in the ratio of  $x:x-1$  moles.

The hydrophobic polyurethane may for example have a hard block content of 20-45%; more preferably 25-35%. The hard block may be derived by reaction of an aromatic diisocyanate with a butane diol. The soft block may be derived from an aromatic diisocyanate and polytetramethylene diol.

One such example will be cited as examples in this specification. Hyphob 1 is an aromatic polyether-urethane, having a hard block content of 26-29%. This material is based upon a polyol of molecular weight 2,000.

As contemplated above, the polymer is produced in a "two-shot" reaction (i.e. the pre-polymer formation step if carried out in the first stage before the extension step is effected in the second step). Alternatively the reaction may be carried out a bulk "one-shot" reaction (i.e. all reactants are mixed together in a single stage reaction).

The invention will now be described further with reference to the following non-limiting examples.



**Example 1**

A glove was made using the following polyurethane and styrene block copolymer formulations:-

**Polyurethane Fluid Medium Formulation:**

		Concentration
Polyurethane Type	Hyphob 1 and Hyphil 2 (7/3 blend ratio)	15% solids in solution
Additive	(1) Precipitated Silica (OK 412)	9 parts per hundred parts polymer solids
	(2) Loxamid OA	5 parts per hundred parts polymer solids
Solvent	Dimethyl Formamide	-
Viscosity (cps)	1000	-

**Styrene Block Copolymer Fluid Medium Formulation:**

		Concentration (wt%)
Block Copolymer	Kraton 1161nu	28
Solvent #1	Toluene	60
Solvent #2	Dimethyl Acetamide	12
Viscosity (cps)	2600	-

A commercially available bisque finished porcelain former was dipped into the polyurethane fluid medium and withdrawn slowly at a speed of 0.25mm / second.

The coated former was dried at 80°C for 9 minutes, allowed to cool to ambient temperature before being dipped into the SIS fluid medium at 2mm / second. The former was withdrawn at 2mm / second and dried at 80°C for 13 minutes.

The warm former was again immersed into the polyurethane solution, withdrawn at 2mm / second and dried at 80°C for a further 9 minutes.

The finished glove showed no cosmetic imperfections, was non-blocking and had excellent dry and damp hand donnability. The glove was unaffected by exposure to a 70:30 isopropyl alcohol / water mixture.

The glove was deemed to be suitable as a surgeons glove.

### Example 2

A glove was made using the following polyurethane and styrene block copolymer formulations:-

Polyurethane Fluid Medium Formulation:

		Concentration
Polyurethane Type	Hyphob 1 and Hyphil 2 (7/3 blend ratio)	15% solids in solution
Additive	(1) Precipitated Silica (OK 412)	9 parts per hundred parts polymer solids
	(2) Loxamid OA	5 parts per hundred parts polymer solids
Solvent	Dimethyl Formamide	-
Viscosity (cps)	1000	-

## Styrene Block Copolymer Fluid Medium Formulation:

		Concentration (wt%)
Block Copolymer	Kraton 1161nu	28
Solvent #1	Toluene	60
Solvent #2	Dimethyl Acetamide	12
Viscosity	2600	-

A commercially available bisque finished surgical glove former was dipped into the polyurethane and withdrawn slowly at 0.75 mm / second.

The coated former was dried at 80°C for 5 minutes, allowed to cool to ambient temperature and dipped into the Kraton 1161 solution. The former was withdrawn at 2mm / second and dried at 80°C for 11 minutes.

The coated warm former was again immersed into the polyurethane solution, withdrawn at 0.75mm / second and dried at 80°C for 5 minutes.

The dried glove was leached in water at 60°C for 5 minutes before being hand stripped and dried in a conventional tumble dryer.

The glove was non blocking and had excellent dry and damp hand donnability. On exposure to a 70:30 isopropyl alcohol / water mixture, the glove showed no evidence of separation. The finished glove showed no signs of cosmetic imperfection at the finger tips. However there was some evidence of small bubbles trapped within the glove, predominantly along the sides of the fingers.

The glove was deemed to be suitable as a powder free examination glove involving the use of alcohol based reagents where minor cosmetic imperfections were not considered to impair the performance of the glove.

**Example 3**

A glove was made using the following polyurethane and styrene block copolymer formulations:-

**Polyurethane Fluid Medium Formulation:**

		Concentration
Polyurethane Type	Hyphob 1	13% solids in solution
Additive	Precipitated Silica (OK 412)	7 parts per hundred parts polymer solids
Solvent	Dimethyl Formamide	-
Viscosity (cps)	900	-

**Styrene Block Copolymer Fluid Medium Formulation:**

		Concentration
Block Copolymer	Kraton 1161nu	32% solids in solution
Solvent	Toluene	-
Viscosity	2800	-

A commercially available bisque finished surgical glove former was dipped into the polyurethane and withdrawn slowly at 0.25 mm / second.

The coated former was dried at 80°C for 5 minutes, allowed to cool to ambient temperature and dipped into the Kraton 1161 solution. The former was withdrawn at 2mm / second and dried at 80°C for 11 minutes.

The coated warm former was again immersed into the polyurethane solution, withdrawn at 0.75mm / second and dried at 80°C for 5 minutes.

The dried glove was leached in water at 60°C for 5 minutes before being hand stripped and dried in a conventional tumble dryer.

The glove was non blocking with good dry hand donnability and showed no signs of degradation or de-lamination after 2 minutes immersion in a 70:30 isopropyl alcohol / water mixture. However, the finished glove had an irregular mottled appearance on the finger region, which was attributed to swelling of the initial polyurethane layer on application of the Kraton layer.

The glove was deemed to be suitable as a powder free examination glove involving the use of alcohol based reagents where minor cosmetic imperfections were not considered to impair the performance of the glove.

#### Example 4

A glove was made using the following polyurethane and styrene block copolymer formulations:-

Polyurethane Fluid Medium Formulation:

		Concentration
Polyurethane Type	Hyphob I	13% solids in solution
Additives	(1) Precipitated Silica (OK 412)	9 parts per hundred parts polymer solids
	(2) Loxamid OA	5 parts per hundred parts polymer solids
Solvent	Dimethyl Formamide	-
Viscosity (cps)	900	-

**Styrene Block Copolymer Fluid Medium Formulation: (as for Example 3)**

A glove was prepared following the same procedure outlined in Example 2.

The glove was non blocking with good dry hand donnability. The glove also possessed a pleasant "silky" feel against the skin and showed no signs of delamination after 2 minutes immersion in a 70:30 isopropyl alcohol / water mixture. However, the finished glove had an irregular mottled appearance, which was attributed to swelling of the initial polyurethane layer on application of the Kraton layer.

The glove was deemed to be suitable as a powder free examination glove involving the use of alcohol based reagents where minor cosmetic imperfections were not considered to impair the performance of the glove.

**Example 5**

A glove was made using the following polyurethane and styrene block copolymer formulations:-

**Polyurethane Fluid Medium Formulation:**

		Concentration
Polyurethane Type	Hyphil 1	17% solids in solution
Additive	Precipitated Silica (OK 412)	9 parts per hundred parts polymer solids
Solvent	Dimethyl Formamide	-
Viscosity (cps)	900	-

**Styrene Block Copolymer Fluid Medium Formulation: (as for Example 3)**

A glove was prepared following the same procedure outlined in Example 2.

The finished glove had no cosmetic defects, which was attributed to the limited amount of swell of the hydrophilic polyurethane in toluene. The glove was non blocking with good dry and damp hand donnability. However, on exposure to a 70:30 isopropyl alcohol / water mixture, the finished glove showed signs of layer separation.

The glove was deemed suitable for use as an examination glove where cosmetic appearance was deemed to be important but no use of alcohol based reagents in the examination procedure was envisaged. Likewise the glove was deemed suitable as a surgeons glove providing no alcohol-based reagents were to be used.

#### Example 6

A glove was made using the following polyurethane and styrene block copolymer formulations:-

Polyurethane Fluid Medium Formulation:

		Concentration
Polyurethane Type	Hyphil 2	19% solids in solution
Additive	Precipitated Silica (OK 412)	9 parts per hundred parts polymer solids
Solvent	Dimethyl Formamide	-
Viscosity (cps)	1200	-

Styrene Block Copolymer Fluid Medium Formulation: (as for Example 3)

A glove was prepared following the same procedure outlined in Example 2.

The finished glove had no cosmetic defects and was non blocking with reasonable dry hand donnability. However, the finished glove showed partial separation after 2 minutes immersion in a 70:30 isopropyl alcohol / water mixture.

The glove was deemed suitable for use as an examination glove where cosmetic appearance was deemed to be important but no use of alcohol based reagents in the examination procedure was envisaged. Likewise the glove was deemed suitable as a surgeons glove providing no alcohol-based reagents were to be used.

#### Example 7

A glove was made using the following polyurethane and styrene block copolymer formulations:-

Polyurethane Fluid Medium Formulation:

		Concentration
Polyurethane Type	Hyphob 1 and Hyphil 2 (4/6 blend ratio)	15% solids in solution
Additive	Precipitated Silica (OK 412)	9 parts per hundred parts polymer solids
Solvent	Dimethyl Formamide	-
Viscosity (cps)	1100	-

Styrene Block Copolymer Fluid Medium Formulation: (as for Example 3)

A glove was prepared following the same procedure outlined in Example 2.



The finished glove had no cosmetic defects, was non blocking and had excellent dry and damp hand donnability. However, on exposure to a 70:30 isopropyl alcohol / water mixture, the glove showed partial separation.

The glove was deemed suitable for use as an examination glove where cosmetic appearance was deemed to be important but no use of alcohol based reagents in the examination procedure was envisaged. Likewise the glove was deemed suitable as a surgeons glove providing no alcohol-based reagents were to be used.

#### Example 8

A glove was made using the following polyurethane and styrene block copolymer formulations:-

##### Polyurethane Fluid Medium Formulation:

		Concentration
Polyurethane Type	Hyphob 1 and Hyphil 2 (7/3 blend ratio)	15% solids in solution
Additive	(1) Precipitated Silica (OK 412)	9 parts per hundred parts polymer solids
	(2) Loxamid OA	5 parts per hundred parts polymer solids
Solvent	Dimethyl Formamide	-
Viscosity (cps)	1000	-

##### Styrene Block Copolymer Fluid Medium Formulation: (as for Example 3)

A glove was prepared following the same procedure outlined in Example 2.

The glove was non blocking and had excellent dry and damp hand donnability. Also on exposure to a 70:30 isopropyl alcohol / water mixture, the glove showed no evidence of separation. However, the finished glove had a mottled appearance at the finger tips.

The glove was deemed to be suitable as a powder free examination glove involving the use of alcohol based reagents where minor cosmetic imperfections were not considered to impair the performance of the glove.

#### Example 9

A glove was made using the following polyurethane and styrene block copolymer formulations:-

Polyurethane Fluid Medium Formulation for initial layer:

		Concentration
Polyurethane Type	Hyphil 2	17% solids in solution
Additive	(1) Precipitated Silica (OK 412)	9 parts per hundred parts polymer solids
	(2) Loxamid OA	5 parts per hundred parts polymer solids
Solvent	Dimethyl Formamide	-
Viscosity (cps)	900	-

## Styrene Block Copolymer Fluid Medium Formulation:

		Concentration (wt%)
Block Copolymer	Kraton 1161nu	24
Solvent #1	Toluene	64
Solvent #2	Dimethyl Acetamide	12
Viscosity (cps)	1900	-

## Polyurethane Fluid Medium Formulation final layer:

		Concentration
Polyurethane Type	Hyphob 1 and Hyphil 2 (7/3 blend ratio)	15% solids in solution
Additive	(1) Precipitated Silica (OK 412)	9 parts per hundred parts polymer solids
	(2) Loxamid OA	5 parts per hundred parts polymer solids
Solvent	Dimethyl Formamide	-
Viscosity (cps)	1000	-

A commercially available bisque finished porcelain former was dipped into the initial polyurethane formulation and withdrawn at 0.75 mm / second.

The coated former was dried at 80°C for 9 minutes, allowed to cool to ambient temperature before being dipped into the SIS solution at 2.5mm / second. The former was withdrawn at 2.5mm / second and dried at 100°C for 13 minutes.

The warm former was immersed into the final polyurethane formulation, withdrawn at 1 mm / second and dried at 100°C for a further 9 minutes.

The glove was leached in water at 60°C before being hand stripped from the former. The glove was inverted on stripping and was re-inverted before being dried in a conventional tumble drier.

The glove had a single wall thickness of 180 microns in the finger and palm areas. The finished glove showed no cosmetic imperfections, was non-blocking and had excellent dry and damp hand donnability. The outer surface of the glove was unaffected by exposure to 70:30 IPA / water.

The glove was deemed suitable as a surgeon's glove to be used when alcohol based reagents were to be used only in contact with the outer glove surface.

#### Example 10

A glove was made using the following polyurethane and styrene block copolymer formulations:-

Polyurethane Fluid Medium Formulation for initial layer:

		Concentration
Polyurethane Type	Hyphil 2	12% solids in solution
Additive	(1) Precipitated Silica (OK 412)	9 parts per hundred parts polymer solids
	(2) Loxamid OA	5 parts per hundred parts polymer solids
Solvent	Dimethyl Formamide	-
Viscosity (cps)	200	-

## Styrene Block Copolymer Fluid Medium Formulation:

		Concentration (wt%)
Block Copolymer	Kraton 1161nu	27
Solvent #1	Toluene	69
Solvent #2	Dimethyl Acetamide	4
Viscosity (cps)	2000	-

## Polyurethane Fluid Medium Formulation final layer:

		Concentration
Polyurethane Type	Hyphil 2	12% solids in solution
Additive	(1) Precipitated Silica (OK 412)	9 parts per hundred parts polymer solids
	(2) Loxamid OA	5 parts per hundred parts polymer solids
Solvent	Dimethyl Formamide	-
Viscosity (cps)	200	-

A commercially available bisque finished porcelain former was dipped into the initial polyurethane formulation at 2.5mm /second and withdrawn at 3.3 mm / second.

The coated former was dried at 80°C for 9 minutes, allowed to cool to ambient temperature before being dipped into the SIS solution at 2.5mm / second. The former was withdrawn at 4.3 mm / second and dried at 100°C for 15 minutes.

The warm former was immersed into the final polyurethane formulation at 2.5 mm / second and withdrawn at 3.3 mm / second and dried at 100°C for a further 9 minutes.

The glove was leached in water at 45°C for 5 minutes before being hand stripped from the former. The glove was inverted on stripping and was re-inverted before being dried in a conventional tumble drier.

The glove had a single wall thickness of 160 microns in the finger and palm areas. The finished glove showed no cosmetic imperfections, was non-blocking and had excellent dry and damp hand donnability. The outer surface of the glove was affected by exposure to 70:30 IPA / water for two minutes and displayed evidence of de-lamination.

The tensile properties of samples cut from gloves made by this method were measured using type 2 dumb-bells (conforming to BS 903: part A2 1995) at a tensile test speed of 500mm / minute. The average of 5 test results is shown below.

Sample thickness (mm)	Force at break (N)	Tensile strength (MPa)	Elongation at break (%)	S <sub>100</sub> Modulus at 100% elongation (MPa)	S <sub>500</sub> Modulus at 500% elongation (MPa)
0.16	12.7	19.7	1330	0.8	1.6

The glove was deemed suitable as a glove to be used when alcohol based reagents were to be used only in contact with the outer glove surface for short periods of time.

**Example 11**

A glove was made using the following polyurethane and styrene block copolymer formulations:-

Polyurethane Fluid Medium Formulation for initial layer:

		Concentration
Polyurethane Type	Hyphil 2	12% solids in solution
Additive	(1) Precipitated Silica (OK 412)	9 parts per hundred parts polymer solids
	(2) Loxamid OA	5 parts per hundred parts polymer solids
Solvent	Dimethyl Formamide	-
Viscosity (cps)	200	-

Styrene Block Copolymer Fluid Medium Formulation:

		Concentration (wt%)
Block Copolymer	Kraton 1161nu	27
Solvent #1	Toluene	69
Solvent #2	Dimethyl Acetamide	4
Viscosity (cps)	2000	-

## Polyurethane Fluid Medium Formulation final layer:

		Concentration
Polyurethane Type	Hyphob 1 and Hyphil 2 (1/1 blend ratio)	8% solids in solution
Additive	(1) Precipitated Silica (OK 412)	9 parts per hundred parts polymer solids
	(2) Loxamid OA	5 parts per hundred parts polymer solids
Solvent	Dimethyl Formamide	-
Viscosity (cps)	120	-

A commercially available bisque finished porcelain former was dipped into the initial polyurethane formulation at 2.5mm /second and withdrawn at 3.3 mm / second.

The coated former was dried at 80°C for 9 minutes, allowed to cool to ambient temperature before being dipped into the SIS solution at 2.5mm / second. The former was withdrawn at 4.3 mm / second and dried at 100°C for 15 minutes.

The warm former was immersed into the final polyurethane formulation at 2.5 mm / second and withdrawn at 3.3 mm / second and dried at 100°C for a further 9 minutes.

The glove was leached in water at 45°C for 5 minutes before being hand stripped from the former. The glove was inverted on stripping and was re-inverted before being dried in a conventional tumble drier.

The glove had a single wall thickness of 160 microns in the finger and palm areas. The finished glove showed no cosmetic imperfections, was non-blocking and



had excellent dry and damp hand donnability. The outer surface of the glove was unaffected by exposure to 70:30 IPA / water for two minutes.

The tensile properties of samples cut from gloves made by this method were measured using type 2 dumb-bells (conforming to BS 903: part A2 1995) at a tensile test speed of 500mm / minute. The average of 5 test results is shown below.

Sample thickness (mm)	Force at break (N)	Tensile strength (MPa)	Elongation at break (%)	S <sub>100</sub> Modulus at 100% elongation (MPa)	S <sub>500</sub> Modulus at 500% elongation (MPa)
0.16	12.7	17.3	1300	0.8	2.4

The glove was deemed suitable as a surgeon's glove to be used when alcohol based reagents were to be used only in contact with the outer glove surface.

#### Example 12

A condom was made using the following polyurethane and styrene block copolymer formulations:-

#### Polyurethane Fluid Medium Formulation

		Concentration
Polyurethane Type	Hyphil 2	18% solids in solution
Additive	(1) Precipitated Silica (OK 412)	9 parts per hundred parts polymer solids
	(2) Loxamid OA	5 parts per hundred parts polymer solids
Solvent	Dimethyl Formamide	-
Viscosity (cps)	800	-

## Styrene Block Copolymer Fluid Medium Formulation:

		Concentration (wt%)
Block Copolymer	Kraton 1161nu	24
Solvent #1	Toluene	70
Solvent #2	Dimethyl Acetamide	6
Viscosity (cps)	1500	-

A commercially available glass condom former was dipped into the polyurethane formulation at 2.5 mm / second and withdrawn slowly at 0.25 mm / second.

The coated former was dried at 80°C for 9 minutes, allowed to cool to ambient temperature before being dipped into the SIS fluid medium at 2.5 mm / second. The former was withdrawn at 1 mm per second at dried at 100°C for 13 minutes.

The warm former was again immersed into the polyurethane formulation at 2.5 mm / second, withdrawn at 0.28 mm / second, and dried at 100°C for 9 minutes.

The condom was leached in water at 60 °C for 5 minutes before being hand stripped. The condom was dried in a conventional tumble drier without the application of powder.

The finished condom had a single wall thickness of 80 microns and a lubricious feel when hydrated. The condom was deemed suitable as a condom with a self-lubricating surface.

**Example 13**

A urinary sheath was made using the following polyurethane and styrene block copolymer formulations:-

**Polyurethane Fluid Medium Formulation**

		Concentration
Polyurethane Type	Hyphil 2	18% solids in solution
Additive	(1) Precipitated Silica (OK 412)	9 parts per hundred parts polymer solids
	(2) Loxamid OA	5 parts per hundred parts polymer solids
Solvent	Dimethyl Formamide	-
Viscosity (cps)	800	-

**Styrene Block Copolymer Fluid Medium Formulation:**

		Concentration (wt%)
Block Copolymer	Kraton 1161nu	24
Solvent #1	Toluene	70
Solvent #2	Dimethyl Acetamide	6
Viscosity (cps)	1500	-

A commercially available stainless steel former was dipped into the polyurethane fluid medium at 2.5 mm / second and withdrawn slowly at a speed of 0.5 mm / second.

The coated former was dried at 80°C for 9 minutes allowed to cool to ambient temperature before being dipped into the SIS fluid medium at 2.5 mm / second. The former was withdrawn at 2 mm / second and dried at 100°C for 11 minutes.

The warm former was again immersed into the polyurethane formulation at 2.5 mm / second, withdrawn at 1 mm / second and dried at 100 °C for 9 minutes.

The urinary sheath was leached in water at 60 °C for 5 minutes before being hand stripped. The urinary sheath was dried in a conventional tumble drier without the application of powder.

The finished urinary sheath had a single wall thickness of 100 microns and a lubricious feel when hydrated. The urinary sheath was deemed suitable for use as a urinary catheter sheath.

#### **Comparative Example 1**

A glove was made using the following styrene block copolymer formulation:-

Styrene Block Copolymer Fluid Medium Formulation: As in Example 3.

A commercially available bisque finished porcelain glove former was dipped into the SIS fluid medium at 2.5 mm / second and withdrawn at 2 mm / second. The coated former was dried at 100°C for 13 minutes before being leached in water at 60°C for five minutes.

On stripping the glove from the former, the glove surfaces stuck together preventing further processing of the product.

#### **Comparative Example 2**

A glove was made using the following polyurethane and styrene block copolymer formulations:-

Polyurethane Fluid Medium Formulation final layer:

		Concentration
Polyurethane Type	Hyphob 1 and Hyphil 2 (7/3 blend ratio)	15% solids in solution
Additive	(1) Precipitated Silica (OK 412)	9 parts per hundred parts polymer solids
	(2) Loxamid OA	5 parts per hundred parts polymer solids
Solvent	Dimethyl Formamide	-
Viscosity (cps)	1000	-

Styrene Block Copolymer Fluid Medium Formulation: As in example 3

A commercially available bisque finished surgical glove former was dipped into the SIS fluid medium at 2.5 mm / second and withdrawn at 2 mm / second. The coated former was dried at 100°C for 13 minutes.

The warm former was immersed into the polyurethane formulation at 2.5 mm / second, withdrawn at 1 mm / second and dried at 100°C for a further 9 minutes. The glove was leached in water at 60°C before being hand stripped from the former.

On stripping from the former the glove surfaces stuck together preventing further processing of the product.

### CLAIMS

1. An elastomeric material having a laminate structure and being comprised of outer layers of a polyurethane composition and an inner layer of a styrene-isoprene-styrene (SIS) or a styrene-butadiene-styrene (SBS) block copolymer or a blend thereof.
2. A material according to claim 1, wherein the material is a tri-laminate structure comprised of an inner SIS or SBS layer or blend thereof and outer polyurethane layers.
3. A material according to claim 1 or 2 wherein the SIS or SBS layer has a thickness of from 30 to 1,000 $\mu$ m.
4. A material according to claim 3 wherein the SIS or SBS layer has a thickness of from 40 to 300 $\mu$ m.
5. A material according to claim 4 wherein the SIS or SBS layer has a thickness of, from 50 to 200 $\mu$ m.
6. A material according to any one of claims 1 to 5 wherein the polyurethane outer layers have a thickness of from 2 to 100 $\mu$ m.
7. A material according to claim 6 wherein the polyurethane outer layers have a thickness of from 5 to 50 $\mu$ m, preferably 10 to 20 $\mu$ m.
8. A material according to any one of claims 1 to 7, wherein the ratio of the thickness of one of the polyurethane layers to the other such layer is in the range 3:1 to 1:3.

9. A material according to any one of claims 1 to 8 wherein the SIS/SBS is a thermoplastic ABA block copolymer elastomer having a styrene content of 15-35% (by weight) and a molecular weight (number average  $M_n$ ) of 150,000-300,000.
10. A material according to claim 9 wherein the SIS/SBS has a molecular weight of 200,000-250,000.
11. A material according to any one of claims 1 to 10 wherein the polyurethane used for the outer layers of the laminate provided, is a hydrophilic polyurethane, a mixture of a hydrophilic polyurethane and a hydrophobic polymer or a hydrophobic polyurethane.
12. A material according to claim 11 wherein the polyurethane composition of at least one of the outer layers of the laminate is comprised of a mixture of a hydrophilic polyurethane and a hydrophobic polymer, preferably a hydrophobic polyurethane.
13. A material according to claim 12 wherein the mixture of a hydrophilic polyurethane and a hydrophobic polymer (preferably a hydrophobic polyurethane) is comprised of from 20% to 60% by weight of the hydrophilic polyurethane and of from 40% to 80% by weight of the hydrophobic polymer.
14. A material according to claim 13 wherein the mixture comprises about 30% of hydrophilic polyurethane and 70% of a hydrophobic polyurethane.
15. A material according to claim 11 wherein one or both of the outer layers contains a hydrophobic polyurethane as the sole polyurethane.
16. A material according to claim 11 wherein one or both outer layers contains a hydrophilic polyurethane as the sole polyurethane.
17. A material according to claim 11 wherein the polyurethane composition of the two outer layers of the laminate is the same or different.

18. An elastomeric article comprised of an elastomeric material according to any one of claims 1 to 17.
19. An elastomeric article as claimed in claim 18 which is a glove, a condom, a catheter or a urinary sheath.
20. An article according to claim 18 or 29, wherein the elastomeric material was produced *in situ* during formation of the article.
21. An article according to any one of claims 18 to 20 produced by dipping of a suitably shaped former firstly into a solution or suspension of a polyurethane, then into a solution or suspension of an SIS or SBS block copolymer, followed by dipping into a solution of a polyurethane (with drying as necessary between the dipping steps) to "build-up" the laminate structure during formation of the article.
22. A method of producing an article according to any one of claims 18 to 21 wherein the article is produced by a dipping process in which an appropriately shaped former is successively dipped into, firstly, a polyurethane-containing solution/suspension, secondly into a SIS or SBS containing solution/suspension, and thirdly into a polyurethane containing solution/suspension.
23. A method according to claim 22 wherein the polyurethane for "dipping" is present in the form of a solution.
24. A method according to claim 23 wherein the solvent for the polyurethane solution is a polar polyurethane solvent.
25. A method according to claim 24 wherein the polar solvent is selected from the group including tetrahydrofuran, methyl ethyl ketone, dimethylformamide, dimethylacetamide, N-methyl pyrrolidone, dimethylsulphoxide, oleic acid amide or mixtures thereof.



26. A method according to claim 25 wherein the solvent is dimethylformamide.
27. A method according to any one of claims 23 to 26 wherein the polyurethane solution comprises 5-20% by weight of the polyurethane.
28. A method according to any one of claims 22 to 27 wherein the solution incorporates precipitated silica.
29. A method according to claim 28 wherein the precipitated silica is present in the solution in an amount of 5-10% by weight of the polyurethane content.
30. A method according to any one of claims 22 to 29 wherein the solution incorporates a fatty acid amide.
31. A method according to claim 30 wherein the fatty acid amide is present in the solution in an amount of 1-10% by weight of the polyurethane content.
32. A method according to any one of claims 22 to 31 wherein the solution incorporates a hard hydrophobic wax material.
33. A method according to claim 32 wherein the hard hydrophobic wax material is present in the solution in an amount of 5-10% by weight of the polyurethane content.
34. A method according to any one of claims 22 to 33 wherein the dipping solution has the following composition:

Polyurethane	15wt%
Dimethylformamide	85wt%
Precipitated Silica	9wt% (based on polyurethane)
Oleic acid amide	5wt% (based on polyurethane)

35. A method according to any one of claims 22 to 33 wherein the initial polyurethane-containing solution/suspension has the following solution/suspension had the following composition:

Polyurethane	12wt%
Dimethylformamide	88wt%
Precipitated Silica	9wt% (based on polyurethane wt)
Oleic acid amide	5wt% (based on polyurethane wt)

36. A method according to any one of claims 22 to 33 or 35 wherein in the third dipping stage the polyurethane containing solution/suspension has the following composition:

Polyurethane	8wt%
Dimethylformamide	92wt%
Precipitated Silica	9wt% (based on polyurethane wt)
Oleic acid amide	5wt% (based on polyurethane wt)

37. A method according to any one of claims 22 to 36 wherein the SIS or SBS is used in the form of a solution.

38. A method according to claim 37 wherein the "dipping" solution contains 20-45% (by weight) of the SIS or SBS block copolymer.

39. A method according to claim 38 wherein the "dipping" solution contains 24-35% (by weight) of the SIS or SBS block copolymer.

40. A method according to claim 38 wherein the solvent for the SIS/SBS solution is an aromatic solvent.

41. A method according to claim 40 wherein the solvent is toluene or xylene.

42. A method according to claim 40 or 41 wherein the polyurethane-containing solutions incorporating a hydrophilic polyurethane and the SIS/SBS solution incorporates a polar liquid which is miscible with the aromatic solvent.

43. A method according to claim 42 wherein the polar liquid is incorporated in the SIS/SBS solution in an amount of 5-20% by weight of the solution.

44. A method according to claim 42 or 43 wherein the polar liquid is chosen from the group including N,N-dimethylamides, e.g. dimethylacetamide or dimethylformamide, ketones, e.g. butan-2-one, or alcohols, e.g. propan-2-ol.

45. A method according any one of claims 40 to 44 wherein the SIS/SBS solution comprises,

SIS	28wt%
Toluene	60wt%
Dimethylacetamide	12wt%

46. A method according to any one of claims 37 to 39 wherein the solvent for the solution is THF.

47. A method according to any one of claims 22 to 46 wherein the first (polyurethane) layer applied to the former is less than 30 microns thick.

48. A method according to claim 47 wherein said thickness is achieved by withdrawal of the former from the polyurethane solution at from 0.2 to 1mm per second.

49. A method according to any one of claims 22 to 48 wherein in the first dipping stage the former is removed from the fluid medium at from 0.05 to 5 mm per second.

50. A method according to claim 49 wherein in the first dipping stage the former is removed from the fluid medium at from 0.2 to 1mm per second.

51. A method according to any one of claims 22 or 50 wherein in the second dipping stage the mould is removed from the fluid medium at from 0.5 to 10 mm per second.

52. A method according claim 51 wherein in the second dipping stage the mould is removed from the fluid medium at from 2 to 5mm per second.

53. A method according to any one of claims 22 to 52 wherein in the third dipping stage the mould is removed from the fluid medium at from 0.2 to 15mm per second.

54. A method according to claim 53 wherein in the third dipping stage the mould is removed from the fluid medium at from 0.5 to 5mm per second.

## INTERNATIONAL SEARCH REPORT

Inte l Application No

PCT/GB 01/02809

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B32B27/30 B32B27/40 B29C41/14 B29C41/22

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B32B B29C C08J A41D A61F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94 20574 A (BAXTER INT) 15 September 1994 (1994-09-15)  page 8, line 21 - line 33	1-5, 11, 17-19, 21, 22
X	US 5 851 683 A (PLAMTHOTTAM SEBASTIAN S ET AL) 22 December 1998 (1998-12-22)  column 4, line 44 - line 55	1-5, 11, 17-19, 21, 22
A	EP 0 854 174 A (ECI MEDICAL TECHNOLOGIES INC) 22 July 1998 (1998-07-22) cited in the application page 2, paragraph 3; claim 1; examples 1, 2	1
A	EP 0 326 033 A (APEX MEDICAL TECH) 2 August 1989 (1989-08-02) claims 1, 4, 5, 7, 8	1

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

\*A\* document defining the general state of the art which is not considered to be of particular relevance

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